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Kinetic study and thermal analysis of the pyrolysis of non-edible oilseed powders by thermogravimetric and differential scanning calorimetric analysis

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ABSTRACT

This work reports the kinetic study of the pyrolysis of four non-edible oil seeds such as Mahua, Karanja, Niger and Linseed conducted at a heating rate of 5, 10 and 15 °C min^{-1} under nitrogen atmosphere. The relation between kinetic parameters and degradation rate was observed with respect to temperature and heating rate. The results indicated that the kinetic parameters were very close to each other and directly proportional to temperature and heating rate. The comparison of kinetic parameters related to heating rate concluded that heating rate had a direct affinity towards activation energy and pre-exponential factor. The TG-DTG analysis indicated three stages of thermal degradation during pyrolysis of the oil seeds whereas DSC analysis point towards the endothermic and exothermic pathway of pyrolysis. The presence of hemicelluloses, cellulose and lignin was determined on the basis of degradation temperature and their respective functional groups in the seeds observed by FTIR analysis.

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1. Introduction

Millions of tons of oil containing seeds of different diversity are available in the world. The advanced utilization of the seeds is to produce most valuable products that may be in the form of biofuels, bio-chemicals or bio-chars. Lignocellulosic biomass is the only source that can be converted to solid, liquid, and gaseous fuels by different thermo-chemical conversion processes. This paper focuses the best use of oil non-edible containing seeds towards the production of bio-oil. The presence of oil in the seeds makes it more convenient feed for the production of bio-oil. Utilization of non-edible oil seed as a source for the production of bio-oil not only fulfills the feed stock requirement but will also provide employment to the rural peoples. Literatures revealed that pyrolysis is one of the profitable techniques to obtain these renewable bio products [1,2]. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analysis are the alternative instrumental techniques which supply significant information regarding pyrolytic behavior of biomass such as decomposition kinetics and the reaction pathway (exothermic or endothermic).

Thermogravimetric analysis (TGA) provides the information regarding the weight loss curve with respect to temperature and time [1,2]. The thermal analysis can be performed in inert atmosphere and oxygen atmosphere to observe the behavior and combustibility of the biomass sample [3–5]. The weight loss data obtained from TGA can be utilized to determine the kinetic parameters such as activation energy, pre-exponential factors, order of the reaction, and ignition temperature and reactivity index (the peak temperature where maximum degradation occurs) of the particular sample [3–5].

Various methods such as Kissinger, Friedman, Flynn-Wall-Ozawa, and Modified Coats-Redfern have been proposed to determine the kinetic parameters by several authors [6–9]. Yao et al. (2008) studied the degradation properties and kinetic parameters of hard wood using all of the above described methods and reported that most of the natural fibers degrades in the temperature range between 215 and 310 °C with apparent activation energy of 160–170 kJ mol^{-1} [6]. However Jiang et al. (2010) and Sasmal et al. (2013) used Kissinger's method to study the kinetic parameters of lignin decomposition [7,8]. Esin et al. (2001) suggested that the entire thermal degradation takes place in the active pyrolytic zone and higher ash content in the biomass results in more amount of residue [9]. Al-Harahsheh et al. (2011) suggested that the presence of minerals and inorganic matters in the biomass enhance the rate of degradation [10]. However the total composition of biomass affects the rate of degradation [11,12]. Biomass comprising with lower lignin and higher cellulose content enhances the degradation rate

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during fast pyrolysis [13]. It was noticed that cellulose degrades within 315–400 °C while hemicellulose degrades at 220–315 °C and lignin decomposition takes place at higher temperature (500–900 °C) [12].

Differential scanning calorimetry is one of the accepted techniques used to determine the heat flow through the sample with respect to temperature. This method offers the heat flow profile due to the difference in the amount of heat required to increase or decrease the temperature of a sample and reference, with respect to temperature. During the experiment nearly same temperature is maintained between the sample and reference. Usually, the temperature profile for a DSC analysis is scheduled such that the sample holder temperature rises linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow through it than the reference to maintain both at the same temperature. DSC analysis provides quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes.

The present study was carried out on four different non-edible oil containing seeds such as Mahua, Karanja, Niger and Linseed. Mahua (*Madhuca indica*) plant is commonly available in forests. The potentiality of this tree in India is 500 000 t of seed and oil potential is about 180 000 t. Mahua seed contains 35% oil and 16% protein. The tree reproduces through seed and coppice. The seed germination takes place in about 10 days. Karanja (*Pongamia pinnata*) is the species of genus *Pongamia*, available in India and other parts of the world. The suitable propagating time is April to June in India and the seed yield per tree ranges from about 10 kg to more than 50 kg. The seed contains 30–40% oil. The Seed collection season in India is from December to April. The plant Niger (*Hyoscyamus niger*) flowers in the month of July and the seed are collected in August. The seed contains 25–35% oil. Linseed (*Linum)* is a quickly grown plant generally harvested after winter season. It is sown in the month of March or April. The seeds contain 30–40% of fixed oil. The details availability and use of the seed and seed oil is discussed elsewhere in literature [14].

The kinetic parameters such as activation energy and pre-exponential factor were determined by TGA method on the basis of their heating rate. Kinetic analysis helps in the design of pyrolyzer, to determine the degradation profile and thermal stability of the respective biomass. Moreover, this analysis also helps to choose efficient pre-treatment techniques to produce fermentable sugars from lignocellulosic biomass towards the production of liquid fuels such as bio-ethanol, bio-butanol etc. The seed materials were characterized by TGA/DTG analysis for their cellulose, hemicelluloses and lignin content where FTIR analysis supported the presence of hemicelluloses, cellulose and lignin in the seeds. The exothermic and endothermic behavior of the seed materials was determined from the DSC analysis.

2. Experimental methods

The oil containing seed samples (Mahua, Karanja, Niger and Linseed) were collected from various locations of Odisha, India. Prior to the experiments, the samples were sundried for 10–12 h and grinded to <1 mm size particle and stored in air-tight polyethylene bags.

2.1. Thermogravimetric analysis

The thermogravimetric experiment was carried out using a thermogravimetric analyzer (Mettler Toledo, Switzerland; TGA851e/LF/1100). About 10 mg of sample was placed in a hemispherical platinum crucible and heated at 5, 10, 15 °C min^{-1} from room temperature to 700 °C to observe the effect of rate of heating on thermal degradation of biomass under nitrogen atmosphere with a flow rate of 40 mL min^{-1}. Less than 1 mm particle sized materials were used because particle size has a significant effect on pyrolysis [15]. Using Arrhenius equation and assuming the reaction of order one; the kinetic parameters like apparent activation energy and average pre-exponential factors were calculated.

2.2. Theory of kinetic analysis

The temperature dependency of reaction rate constant is represented by Arrhenius law which states that

$$k = k_o \cdot e^{-(E/RT)} \tag{1}$$

The terms k, k_o, E, R and T are the reaction rate constant, pre-exponential factor, activation energy, gas constant and temperature respectively.

The Arrhenius expression can be written as a function of temperature and conversion as expressed in the Eq. (2).

$$\frac{dX}{dt} = k_o \cdot e^{-\left(\frac{E}{RT}\right)} \cdot f(X) \tag{2}$$

where X is the conversion and dX/dt represents the conversion with respect to time.

Now consider that the initial weight of the sample taken in the crucible for the experiment is W_o. The weight of the sample after heating at a particular time and temperature is W and the final weight remaining at the end of the process is W_f.

The conversion at certain temperature (X) can be calculated by the ratio of the difference between the initial and remaining weight of the sample to the difference of the initial and final weight of the sample. The mathematical form of the conversion (X) can be written as

$$X = \frac{(W_0 - W)}{\left(W_o - W_f\right)} \tag{3}$$

here, $f(X)$ represents the function related with conversion ratio X, which depends on the reaction mechanism of pyrolysis. For simple reactions, we can write $f(X) = (1 - X)^n$ where n is the order of the reaction [16].

During thermogravimetric analysis the heating rate was considered as dT/dt and denoted by β. Now, Eq. (2) can be written in the form of heating rate as follows

$$\frac{dX}{dT} = \frac{k_o}{\beta} \cdot e^{-\left(\frac{E}{RT}\right)} \cdot (1 - X)^n \tag{4}$$

$$\Rightarrow \frac{dX}{(1 - X)^n} = \frac{k_o}{\beta} \cdot e^{-\left(\frac{E}{RT}\right)} \cdot dT \tag{5}$$

here for Eq. (4): $dX/dt = (dX/dT) \times (dT/dt)$, where β is the scan rate $= dT/dt$.

Literature states that formation of more amounts of non condensable gas/volatiles is due to the secondary reaction takes place during pyrolysis [17] which may be of higher order. Pyrolysis of biomass produces maximum liquid yield during primary reaction. Hence, assuming the order of the reaction one and integrating the Eq. (5), we will get

$$-\mathrm{Ln}(1 - X) = \frac{k_o}{\beta} \cdot \frac{RT^2}{E} \cdot e^{-\left(\frac{E}{RT}\right)} \tag{6}$$

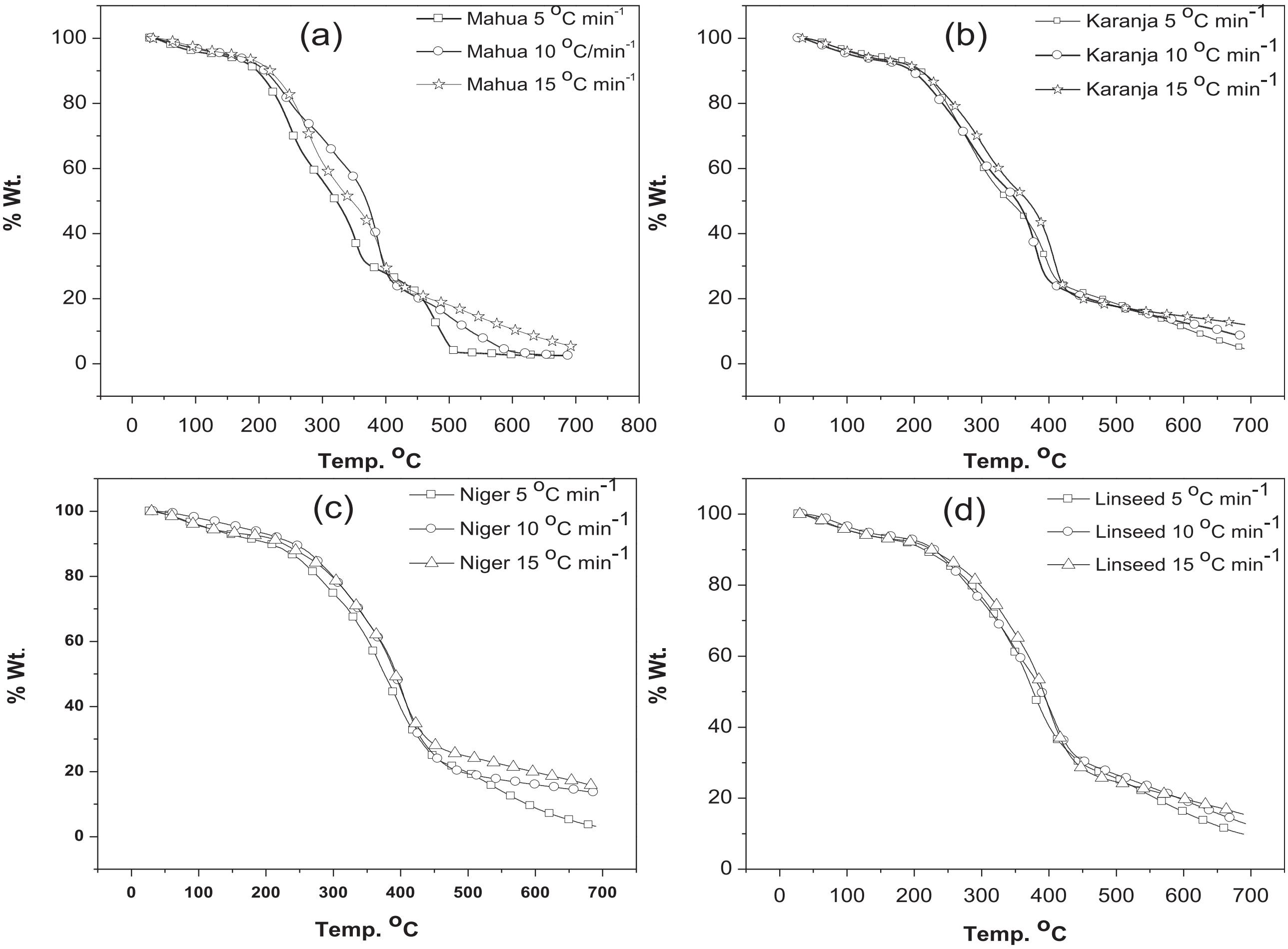

Fig. 1. Effect of rate of heating on weight loss for (a) Mahua seed, (b) Karanja seed, (c) Niger seed, (d) Linseed seed.

for better understanding taking the natural logarithm of both sides of the above equation, the Eq. (6) will become

$$\mathrm{Ln}(-\mathrm{Ln}(1-X)) = \mathrm{Ln}\frac{k_o}{\beta}\cdot\frac{RT^2}{E}-\frac{E}{RT} \tag{7}$$

This equation was used to determine the kinetic parameters of the biomass samples. The plot between Ln(−Ln (1 − X)) vs. (1/T) give a straight line and the slope represents the value of (E/R) and the intercept will offer the value of Ln[(k_o/β)·(RT^2/E)]. The value of the pre-exponential factor k_o can be calculated by substituting the value of β, R, T and E. This method was also used to determine the Arrhenius parameters by Parekh et al. (2009) [18].

2.3. Differential scanning calorimetric analysis

DSC experiments were carried out in a METTLER TOLEDO DSC 1 star^e system analyzer at a heating rate of 10 °C min^{-1} from 25 to 450 °C under N_2 atmosphere at a constant flow rate of 40 mL min^{-1} to remove gaseous products produced during the analysis. The powdered seed samples were taken in an aluminum crucible (40 μL) covered by a perforated lid which helps to escape the formed gases freely and DSC thermograms were collected as function of temperature and heat flow (Q).

2.4. Moisture analysis

The moisture content is defined as the amount of water present per unit mass of dry solid. About 1 g of seed material was dried in an oven for 1 h at 105 °C temperature; the weight loss of the sample provides the percentage of moisture in the respective samples.

$$\mathrm{Moisture}(\%) = \left(\frac{\text{Weight of initial biomass} - \text{Weight of dried biomass}}{\text{Weight of initial biomass}}\right)\times 100 \tag{8}$$

2.5. FTIR analysis

The FTIR analyses of the raw materials were executed using Excalibur Bio-Rad spectrophotometer (Model FTS 3500 GX) attached with DRS (Diffuse Reflectance Spectroscopy). Oven dried (100 °C for 1 h) powdered KBr was mixed with the samples at a ratio of 1:100 and loaded in the sample holder and the IR spectra were collected at scan rate of 40 with a step size of 4 cm^{-1} within the range of 400–4000 cm^{-1}. Before the sample analysis, base line FTIR spectra of KBr were employed.

3. Results and discussions

3.1. Thermogravimetric analysis

The thermogravimetric analysis of the seed materials were carried out at a heating rate of 5, 10 and 15 °C min^{-1} respectively and the weight loss curves with respect to temperature and time were collected. Figs. 1 and 2 shows the thermal degradation related to temperature and time. From Fig. 1 it was clear that during thermal degradation the seed materials undergone three different stages.

Initially for all the cases within 200 °C, the evolution, not the degradation of moisture and other trapped volatile compounds takes place in this temperature range. Degradation does not significant until temperature increases above 200 °C. Thus, as shown in Fig. 3, large increases occur for 'dWt/dt' at temperatures in the range 200–500 °C for all four oil seeds at all three scan rates. The remaining char materials degrade slowly up to the final temperature (700 °C). Only in case of Mahua seed the second stage degradation continued up to 488 °C at the rate of 5 °C min^{-1} whereas for all seeds at all heating rates the second stage was completed within 400 °C. At this heating rate most of volatiles were removed within 488 °C. Hence at the heating rate of 5 °C min^{-1}, a little weight loss occurred within 500–700 °C. This confirmed that low heating rate enhanced the conversion rate with high residence time (Figs. 1 and 2). However at higher heating rate, the rate of weight loss continued up to 700 °C beyond active pyrolytic zone. The second stage of degradation is known as active pyrolytic zone where maximum volatilization takes place [1,2]. During this stage the intermolecular association and weaker chemical bonds break. Because of the lower temperature the side aliphatic chains may break and small gaseous molecules form. In third stage, higher temperature chemical bond may break and the higher molecular weight compounds convert to lower molecular weight compounds and at the end char materials remain as residue which can be used as solid fuel and bio-adsorbent [16,18]. The volatiles can be collected in the form of condensed liquid which can be used as fuel and for the production of bio-chemicals [1,2]. The third stage of degradation continues very slowly as shown in Fig. 1. The degradation profiles of three main components present in biomass, viz. hemicellulose, cellulose and lignin with respect to temperature can be seen from the DTG thermographs (Fig. 3). As per literature

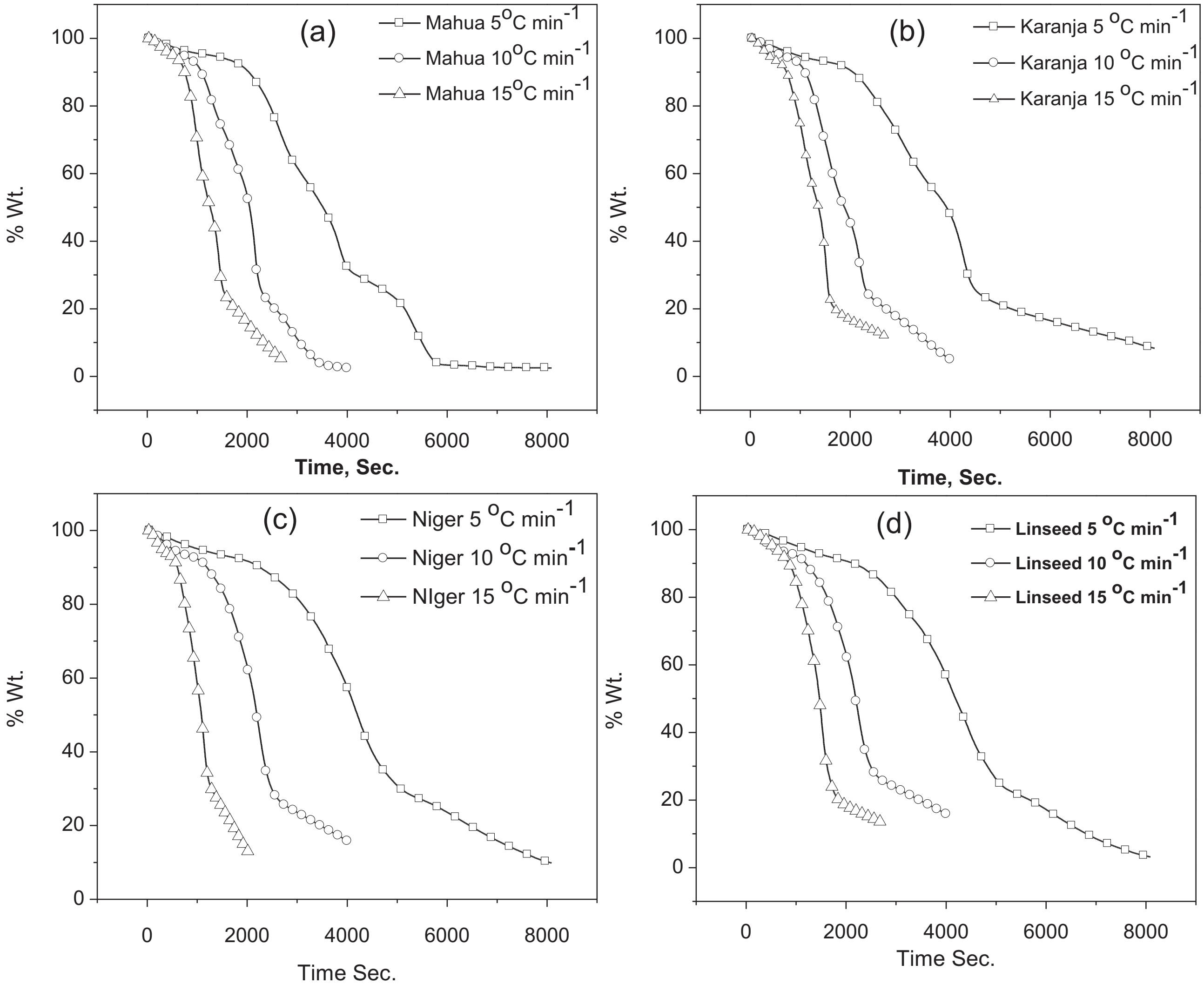

Fig. 2. Effect of rate of heating on degradation time for (a) Mahua seed, (b) Karanja seed, (c) Niger seed, (d) Linseed seed.

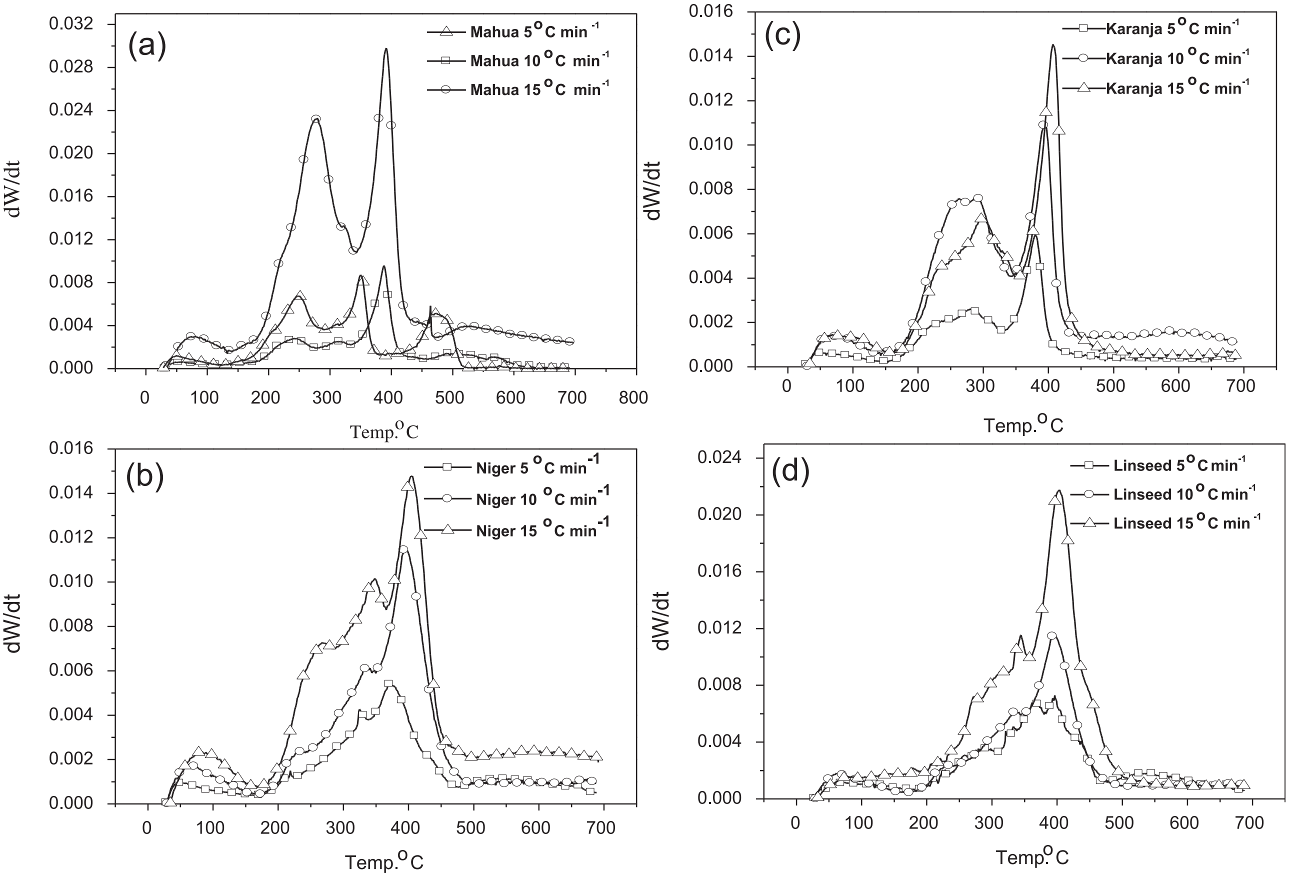

Fig. 3. DTG thermograph at different rate of heating for (a) Mahua seed, (b) Karanja seed, (c) Niger seed, (d) Linseed seed.

hemicelluloses degrades at lower temperature followed by cellulose and lignin [13,19].

The weight loss below 100 °C was due to the evaporation of more volatile compounds and moisture. The water content was removed in between 100–130 °C, 130–250 °C for volatile compounds, 250–350 °C for hemicelluloses, 350–500 °C for cellulose and lignin degrades above 500 °C [15]. Generally, lignin degrades at higher temperature due to higher thermal stability. The phenolic hydroxyl group which represents lignin (as observed from the FTIR analysis) increases the stability of lignin and hence lignin degrades at high temperature. The DTG thermograph shows the rate of degradation with respect to temperature which describes the degradation of hemicelluloses, cellulose and lignin. The results concluded that four stages of degradation were observed for Mahua and Karanja seeds where as a three stage degradation was observed for Niger and Linseed seeds. The first stage of degradation may be due to the removal of both moisture and extractives [16]. Second stage denotes the devolatilization of hemicelluloses and in the third stage the cellulose degrades and lignin degrades slowly at higher temperature till the end. The presence of lignin is the cause of production of char that was the product at the end of the pyrolysis process [16].

3.2. Effect of heating rate in thermal degradation

The effect of heating rate on weight loss is visualized in Figs. 1 and 2. The time of reaction decreases with increase in heating rate (Fig. 2). At lower heating rate well degradation of cellulose and

Table 1
Stages of thermal degradation with respect to temperature observed from DTG thermograph.

Seeds	Heating rate °C min^{-1}	1st stage temperature range, °C	2nd stage temperature range, °C	3rd stage temperature range, °C	4th stage temperature range, °C	Remaining char, %
Mahua	5	Up to 128	128–300	270–387	370–700	2.37
	10	Up to125	125–286	323–430	430–700	2.47
	15	Up to 120	120–333	333–422	422–700	5.08
Karanja	5	Up to 160	160–320	320–410	410–700	0.78
	10	Up to 160	160–335	335–428	428–700	4.59
	15	Up to 160	160–343	343–450	450–700	11.98
Niger	5	Up to 180	180–460	460–700	–	3.39
	10	Up to 180	180–470	470–700	–	9.85
	15	Up to 180	180–490	490–700	–	12.77
Linseed	5	Up to 160	160–460	460–700	–	3.16
	10	Up to 160	160–470	470–700	–	13.49
	15	Up to 170	170–360	360–700	–	15.47

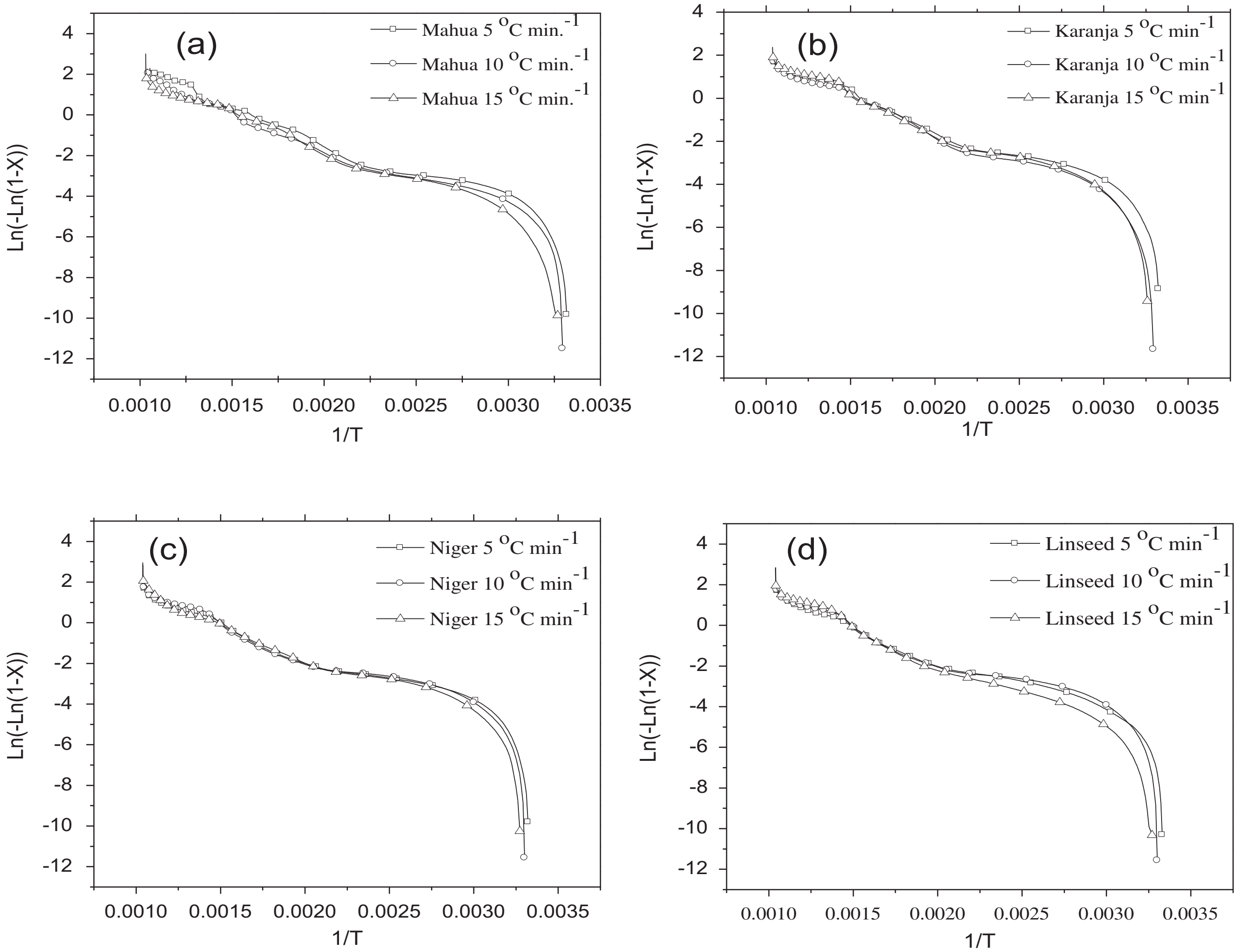

Fig. 4. The plot between [Ln(−Ln (1 − X)) vs. (1/T)].

hemicelluloses take place [20]. The pyrolytic curves of all the four seeds confirms that heating rate is directly proportional to the rate of degradation and from literature it was found that pyrolysis at higher heating rate results more yield of liquid [9]. The rate of degradation also increases for hemicelluloses, cellulose and lignin with increase in heating rate as was evident from the DTG thermographs. The increase in the rate of degradations might be due to the increasing the heating rate and presence of some minerals like potassium and magnesium [9,13]. The rise in the temperature with heating rate not only increases the rate of weight loss but also changed the temperature range for degradation (Table 1). From Table 1 it was observed that the percentage of the char yield increased with heating rate, because at higher heating rate the time of pyrolysis decreased.

Table 2
Linear equation obtained from the plot between Ln(−Ln (1 − X)) vs. (1/T).

	Mahua seed		Karanja seed		Niger seed		Linseed	
Rate of heating	Equation	R^2	Equation	R^2	Equation	R^2	Equation	R^2
5 °C min^{-1}	$y = -3436 \cdot x + 5.582$	0.966	$y = -2994 \cdot x + 4.65$	0.968	$y = -2944 \cdot x + 4.329$	0.948	$y = -3063 \cdot x + 4.509$	0.957
10 °C min^{-1}	$Y = -3395 \cdot x + 5.196$	0.965	$y = -3234 \cdot x + 4.878$	0.955	$y = -3070 \cdot x + 4.581$	0.934	$y = -3070 \cdot x + 4.581$	0.934
15 °C min^{-1}	$y = -3483 \cdot x + 5.234$	0.964	$y = -3265 \cdot x + 5.081$	0.966	$y = -3128 \cdot x + 4.623$	0.953	$y = -3671 \cdot x + 5.493$	0.96

Table 3
Kinetic parameters at different rate of heating.

Name of the seeds	Apparent activation energy at different rate of heating E (kJ mol^{-1})			Average pre-exponential factor at different rate of heating, k_o (s^{-1})		
Heating rate	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}
Karanja	24.9	26.6	27.1	277.9	375.8	467.6
Mahua	28.2	28.8	29.1	590.5	623.2	656.2
Niger	24.1	25.4	26.3	223.3	262.4	302.1
Linseed	25.1	29.9	30.1	241.1	726.1	774.2

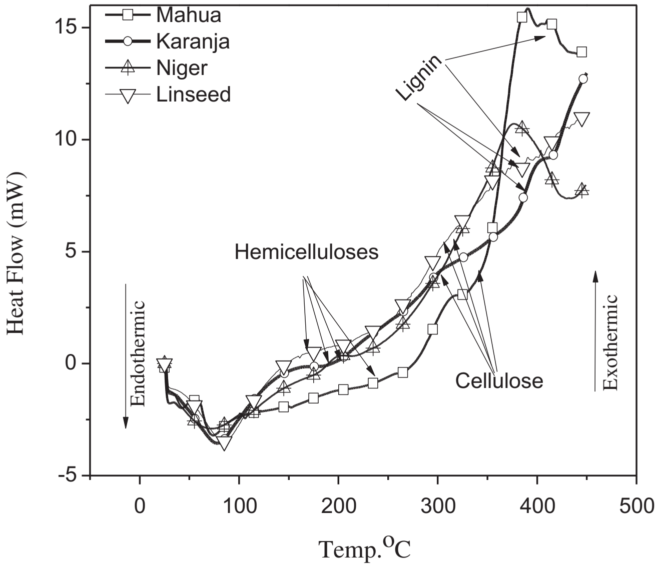

Fig. 5. DSC thermograph of non-edible oil seeds.

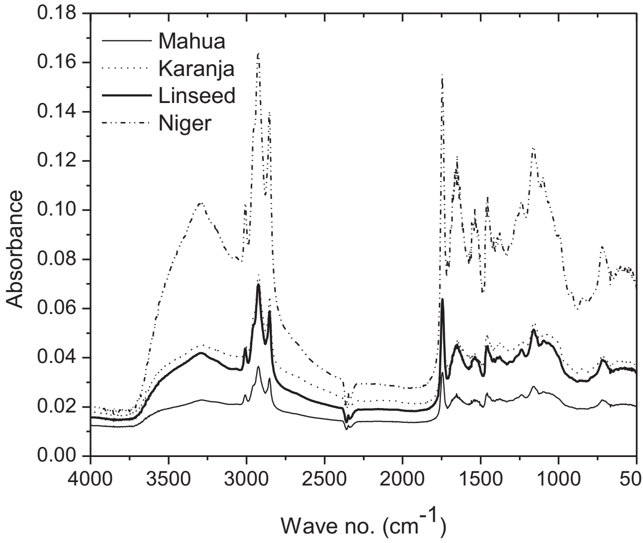

Fig. 6. FTIR spectra of the non-edible oil seeds.

3.3. Analysis of kinetic parameters

The apparent activation energy and average pre-exponential factor at different heating rate was calculated using the integral form of Arrhenius equation from the TGA data. The linear equations and R^2 values observed from the plot between Ln(−Ln (1 − X)) vs. (1/T) (Fig. 4) for each seed samples is described in Table 2. The data were analyzed over the '1/T' range from 0.0010 to 0.0030. Also, the R^2 data in this table indicated that the equations are nearly linear in behavior. This suggests that the kinetics of pyrolysis were not first-order over the entire temperature range.

The slope of the equations was used to calculate the activation energy where intercept provides the value of $\mathrm{Ln}[(k_o/\beta)\cdot(RT^2/E)]$ and used to calculate pre-exponential factor. The pyrolysis kinetic parameters of the seed materials are presented in Table 3. The comparison study confirmed that the value of activation energy for all of the non-edible oil seeds were closer to each other (Table 3). It was observed that rate of reaction is directly proportional to the heating rate. This may be the caused by difference in biochemical composition, heat transfer and mass transfer effect [16,20].

3.4. DSC analysis

Fig. 5 illustrates the DSC analysis of the seed materials. The main properties measured by DSC analysis is heat flow, the flow of energy into or out of the sample as a function of temperature or time, and usually shown in units of mW on the y-axis.

When sample undergoes physical transformation such as phase transition, more or less heat is required to maintain both the sample and reference at the same temperature. The heat flow to the sample depends on the process whether it is exothermic or endothermic. The DSC curves showed that the seed endured an endothermic transition as temperature increased to ~100 °C, followed by a continuous exothermic transition from 80 °C to 400 °C. The degradation offers exothermic peak because during pyrolysis heat was provided continuously till the end of the process [17]. Due to the presence of moisture (Table 4) heat was absorbed by the material and an endothermic pathway was obtained up to 80 °C [21]. The heat was released from the material and the reaction pathway changed from endothermic to exothermic when the temperature exceeded 80 °C.

Table 4
Moisture content of seed material after 10–12 h sun drying.

Seeds sample	Moisture content, %
Mahua	5.65
Karanja	7.27
Niger	5.97
Linseed	6.53

3.5. Determination of functional group using FTIR analysis

The presence of cellulose, hemicelluloses and lignin was confirmed by FTIR analysis which shows the respective functional groups. Fig. 6 shows the FTIR spectra of the non-edible oil seeds.

The peak observed in the range of 1710–1740 cm^{-1} shows the presence of carbonyl group like ester (C=O) which gives an evidence of hemicelluloses in the samples. The peak observed in the range of 1400–1500 cm^{-1} was due to the symmetric deformation of CH_2 group of cellulose and the connection with the asymmetric deformation of C—O—C (1167.24 cm^{-1}) of the cellulose and hemicelluloses which is related to the presence of C—OH stretching vibrations. The band detected at 1500–1700 cm^{-1} and 3200–3400 cm^{-1} refers to C=C aromatic ring and phenolic hydroxyl group (O—H) due to the presence of moisture, lignin and protein contents in the seed materials [15,21–23]. FTIR analysis confirmed the presence of cellulose, hemicelluloses and lignin as indicated by the absorbance peak. The TG analysis results indicated a three step thermal degradation of all the four biomasses corresponded to hemicelluloses, cellulose and lignin. The DSC analysis also confirmed that the degradation process was endothermic followed by exothermic. The endothermic process was attributed to the presence of moisture whereas the exothermic process resulted due to the distinct presence of hemicelluloses, cellulose and lignin. Thus, FTIR, TG and DSC analysis confirmed the presence of three major components of the biomasses viz. hemicelluloses, cellulose and lignin along with moisture.

4. Conclusion

Thermogravimetric and differential scanning calorimetric analysis were performed to observe the kinetic properties during pyrolysis of oil containing seeds such as Mahua, Karanja, Niger and Linseed. The pyrolytic behavior of these seeds at different heating rate was determined and the kinetic parameters showed that the seeds had very close activation energy among them. The comparison of kinetic parameters related to heating rate concluded that heating rate had a direct affinity towards activation energy and pre-exponential factor. Higher heating rate constrain faster decomposition with short residence time. The comparison between TGA and DSC analysis confirmed that the pyrolysis reaction proceeded at three different steps. From DSC analysis, it was clear that the evolution of moisture resulted in endothermic peak whereas hemicellulose, cellulose and lignin provided the exothermic peak. The presence of cellulose, hemicelluloses and lignin was also confirmed by their respective functional groups as determined from FTIR analysis. The results from the present study will help in designing of a continuous pyrolyzer to produce value-added products from various oil containing seeds.

Nomenclature

k_o	pre-exponential factor, s^{-1}
T	pyrolysis temperature, K
E	activation energy, kJ mol^{-1}
W	weight of sample at time ‘t’, mg
k	pyrolysis rate constant, s^{-1}
W_o	initial weight of sample, mg
n	reaction order
W_f	final weight of sample, mg
R	gas constant $= 8.314$ J g mol^{-1} K^{-1}
X	conversion of samples
t	pyrolysis time, s
Q	heat flow, mW

References

[1] Singh RK, Shadangi KP. Liquid fuel from castor seeds by pyrolysis. Fuel 2011;90:2538–44.

[2] Shadangi KP, Singh RK. Thermolysis of polanga seed cake to bio-oil using semi batch reactor. Fuel 2012;97:450–6.

[3] Ghetti P, Ricca L, Angelini L. Thermal analysis of biomass and corresponding pyrolysis products. Fuel 1996;75:565–73.

[4] Dimitrakopoulos AP. Thermogravimetric analysis of Mediterranean plant species. J Anal Appl Pyrolysis 2001;60:123–30.

[5] Kumara A, Wanga L, Dzenisc YA, Jonesa DD, Hannaa MA. Thermogravimetric characterization of corn stover as gasification and pyrolysis feedstock. Biomass Bioenerg 2008;32:460–7.

[6] Yao F, Wu Q, Lei Y, Guo W, Xu Y. Thermal decomposition kinetics of natural fibers: activation energy with dynamic thermogravimetric analysis. Polym Degrad Stab 2008;93:90–8.

[7] Jiang G, Nowakowski DJ, Bridgwater AV. A systematic study of the kinetics of lignin pyrolysis. Thermochim Acta 2010;498:61–6.

[8] Sasmal S, Goud VV, Mohanty K. Determination of salutary parameters to facilitate bio-energy production from three uncommon biomasses using thermogravimetric analysis. J Therm Anal Calorim 2013;111:1649–55.

[9] Ceulcuoglu E, UE Nay E, Karaosmanoglu F. Thermogravimetric analysis of the rapeseed cake. Energ Sourc 2001;23:889–95.

[10] Al-Harahsheh M, Al-Ayed O, Robinson J, Kingman S, Al-Harahsheh A, Tarawneh K, et al. Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales. Fuel Process Technol 2011;92:1805–11.

[11] Yang H, Yan R, Chen H, Lee DH, Zheng C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 2007;86(12–13):1781–8.

[12] Gottipati R, Mishra S. A kinetic study on pyrolysis and combustion characteristics of oil cakes: effect of cellulose and lignin content. J Fuel Chem Technol 2011;39(4):265–70.

[13] Chen W, Kuo P. Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis. Energy 2011;36:6451–60.

[14] Shadangi KP, Mohanty K. Characterization of nonconventional oil containing seeds towards the production of bio-fuel. JRSE 2013;5:033111–3.

[15] Naik S, Goud VV, Rout PK, Jacobson K, Dalai AK. Characterization of Canadian biomass for alternative renewable biofuel. Renew Energ 2010;35:1624–31.

[16] Zhang X, Xu M, Sun R, Sun Li. Study on biomass pyrolysis kinetics. J Eng Gas Turbine Power 2006;128:493.

[17] Velden MV, Baeyens J, Brems A, Janssens B, Dewi R. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. Renew Energ 2010;35:232–42.

[18] Parekh DB, Rotliwala YC, Parikh PA. Synergetic pyrolysis of high density polyethylene and Jatropha and Karanj cakes: a thermogravimetric study. IRESR 2009;1:033107.

[19] Guo J, Lua AC. Kinetic study on pyrolysis of extracted oil palm fiber isothermal and non-isothermal conditions. J Therm Anal Calorim 2000;59:763–74.

[20] Yang H, Yan R, Chin T, Liang DT, Chen H, Zheng C. Thermogravimetric analysis-fourier transform infrared analysis of palm oil waste pyrolysis. Energ Fuel 2004;18:1814–21.

[21] Moran JI, Alvarez VA, Cyras VP, Vazquez A. Extraction of cellulose and preparation of nanocellulose from sisal fibers. Cellulose 2008;15:149–59.

[22] Mothe CG, Miranda de IC. Characterization of sugarcane and coconut fibers by thermal analysis and FTIR. J Therm Anal Calorim 2009;97:661–5.

[23] Sasmal S, Goud VV, Mohanty K. Characterization of biomasses available in the region of North-East India for production of biofuels. Biomass Bioenerg 2012;45:212–20.